

Fabrication of Boronized Ti6Al4V/HA Composites by Microwave Sintering in Mixed Gases

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Cite This: *ACS Omega* 2020, 5, 11629–11636



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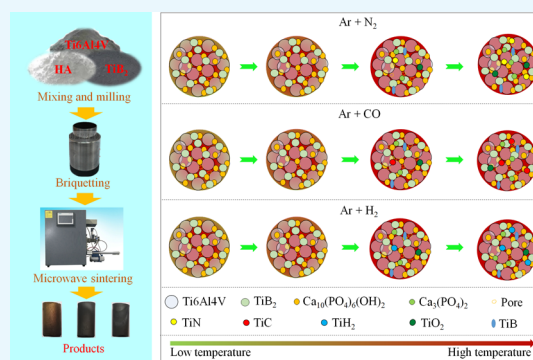
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ABSTRACT: The effect of atmosphere on the fabrication of boronized Ti6Al4V/hydroxyapatite (HA) composites was investigated by microwave sintering of the mixture of Ti6Al4V alloy, HA, and TiB₂ powders at 1050 °C for 30 min in the mixed gases of Ar + N₂, Ar + CO, and Ar + H₂, respectively. The presence of N₂, CO, and H₂ in the atmosphere caused formations of TiN, TiC, and TiH₂ in the composites, respectively, together with evident microstructural changes that determined the mechanical properties (compressive strength, compressive modulus, and Vickers microhardness) and wettabilities of the composites after sintering. It was found that the composite exhibited the best mechanical performance with compressive strength of 148.59 MPa, compressive modulus of 13.9 GPa, and Vickers microhardness of 300.39 HV by microwave sintering in the mixed gas of Ar + H₂, followed by those obtained in the mixed gases of Ar + N₂ and Ar + CO.

All of the composites possessed desirable wettabilities, irrespective of the sintering atmosphere, as demonstrated by their very low water contact angles ($\leq 31.9^\circ$). The results indicated that it is critical to control the extents of nitration and carbonization for maintaining the performance of the composites, especially the mechanical properties, whereas there is no strict requirement for the same objective using the mixed gas of Ar + H₂ in which qualified composites could be obtained for implant applications.



1. INTRODUCTION

As a superior biomaterial and a main component of natural bone,¹ hydroxyapatite has been receiving increasing interest in hard-tissue restoration, benefiting from its capability in accelerating bone growth.² It is characterized by good bioactivity and excellent osteoconductive properties attributed to its chemical and crystallographic features, which, however, simultaneously result in poor mechanical properties.³ Because of these characteristics, individual HA is normally used in fabricating implants with no or low load, such as graft materials. Its use in many typical load-bearing implants, e.g., artificial teeth, is still challenging.⁴

To remedy the above shortcomings of HA, it is considered effective to incorporate biocompatible high-strength metals (as matrix) to HA to produce biocomposites with a good combination of bioactivity and mechanical reliability.^{4,5} Among these metals, titanium and its alloys (e.g., Ti6Al4V) are deemed as the most promising candidates because of their properties (e.g., Young's modulus) that closely resemble those of bone⁶ and of their most biocompatible features.⁷ However, due to distinctly different natures between the metal and ceramic (HA), the mechanical properties of the composites prepared by traditional methods, such as sintering, usually require further enhancement. To improve the properties of these materials, some additives may be used. For instance, a small amount of TiB₂ (~5 wt %) may be added to the mixture

of titanium/titanium alloy and HA to induce its reaction with Ti during sintering for the production of TiB, which bonds the composite components, thereby improving the mechanical performance of the composites.⁸ In general, the sintering process is carried out in a vacuum,⁹ protective, or inert atmosphere (typically Ar) to prevent adverse reactions such as oxidation of titanium.^{4,5} It was also reported that nitriding could enhance the wear resistance of the titanium alloy.¹⁰ Sintering of the composites in a mixed gas consisting of Ar and a small amount of N₂ (e.g., ~3 vol %) may have a great influence on the composition, microstructure, and thus the mechanical performance and bioactivity of the composites.¹¹ A few studies also showed that the residual oxygen in the commercial Ar gas usually causes the formation of titanium oxide on the sample surface, which will lower the biocompatibility and mechanical properties of the resulting composites.^{12,13} From this perspective, the introduction of reducing gases, such as CO and H₂, to Ar to obtain a mixed gas

Received: February 26, 2020

Accepted: April 27, 2020

Published: May 12, 2020



for sintering may be helpful. Additionally, the decomposition of HA can be inhibited via heating in an atmosphere containing CO.¹⁴ Obviously, it is essential to evaluate the effect of atmosphere consisting of Ar and different gases on the sintering process, which has not yet been reported systematically.

The aim of this study was to explore the fabrication of boronized Ti6Al4V/HA composites in different mixed gases (Ar + N₂, Ar + CO, and Ar + H₂), which was based on sintering of the compacts of mixed Ti6Al4V, HA, and TiB₂ powders under microwave irradiation. Microwave energy was applied for the process in view of its distinct advantages over the other sintering methods, including volumetric and selective heating,^{15–17} and of the good microwave absorption capabilities of Ti6Al4V and TiB₂ powders.^{18,19} The impacts of atmosphere on phase compositions, microstructures, densities/porosities, compressive strength, compressive moduli, Vickers microhardness, and water contact angles of the resulting composites have been evaluated. It was found that the sintering atmosphere played a significant role in determining the mechanical properties and wettability of the resulting composites and those produced in the mixed gas of Ar + H₂ have the potential to serve as qualified candidates for implant applications.

2. EXPERIMENTAL SECTION

In this study, commercial Ti6Al4V powder, nanoscale HA powder, and TiB₂ powder were used as raw materials. The Ti6Al4V powder was composed of α -Ti and β -Ti phases, with a purity of 98% and a particle size of 15–50 μ m. It was used for preparing the matrix of the target composites to ensure sufficient strength after sintering.¹¹ The nanoscale HA powder was obtained by the precipitation method. It had a needle-like morphology with an average length and diameter of about 100 and 20 nm, respectively. As the reinforcement agent, the TiB₂ powder with a purity of 98% and a particle size of 4–8 μ m was used. Figure 1 shows the micromorphologies of Ti6Al4V, HA, and TiB₂ powders.

Prior to sintering, 90% Ti6Al4V powder, 5 wt % HA powder, and 5 wt % TiB₂ powder were mixed and milled in a planetary ball mill (XQM-2, Miki Technology Ltd., China) with the

addition of extra 3 wt % stearic acid as a binder at a speed of 200 rpm for a period of 12 h in an argon atmosphere. The dosages of HA and TiB₂ were determined based on the results of the previous studies.^{5,8} During the operation of ball mill, the mass ratio of stainless steel ball to the mixture was 10. Figure 1 shows the micromorphology of the milled mixture with good dispersion of HA and TiB₂. The milled mixture was then briquetted using a hardened steel die at the pressure of 900 MPa, producing cylindrical powder compacts with a diameter of 8 mm and a height of 10 mm. After the obtained compacts were heated in a conventional tube furnace at 380 °C for 2 h in an inert atmosphere for debinding, they were subjected to sintering at 1050 °C for 30 min in a microwave tube furnace (maximum power of 1.4 kW, 2.45 GHz, CY-SVT1200C-SD, Hunan Change Microwave Technology Co. Ltd., China), which was equipped with an advanced PID-based temperature control system. The experiments were carried out in different atmospheres, including Ar + 3 vol % N₂, Ar + 3 vol % CO, and Ar + 3 vol % H₂, by controlling the flow rates of individual gases. The sintering conditions were selected in view of the significant decomposition of HA, which usually occurs at temperatures above 1100 °C.^{4,11} For each test, eight samples were prepared. The sintered samples were subsequently cooled to room temperature and collected as the composite samples for the characterization and analysis of the properties.

The phase compositions of the composite samples were determined using an X-ray diffractometer (XRD, D/max 2550PC, Rigaku Co., Ltd., Japan). The microstructures of the samples were determined using a field-emission scanning electron microscope (FESEM, S4800, SIGMA HD, Nova450, Japan), which was also equipped with an energy-dispersive X-ray spectrometer (EDS). For analysis of the effect of atmosphere on the densification of the samples, their bulk densities and porosities were measured following the rule of the mixture and the Archimedes' principle. The values of the compressive strength of the samples were measured using an electronic universal testing machine (DDL50, Changchun, China) according to the Chinese National Standard Test Method GBT 5072-2008. The compressive moduli of the samples were determined using the same apparatus. The values of the Vickers microhardness of the composite samples were measured using a Vickers hardness tester (VH1150, Wilson, USA) with an operating load of 9.8 N and a dwell period of 10 s in accordance with the ASTM E384-06 standard. For evaluating the effect of atmosphere on the wettability of the samples, the corresponding water contact angles were measured using a contact angle measuring instrument (DSA-30, CRUSS, Germany).

3. RESULTS AND DISCUSSION

Figure 2 shows the XRD patterns of the composites obtained by microwave sintering of the powder mixtures in different atmospheres. It was found that the atmosphere had great influence on the phase compositions of the samples.

In the Ar + N₂ atmosphere, the main phases included original α -Ti (hcp) and β -Ti (bcc) phases in the titanium alloy as well as TiN.²⁰ In particular, the presence of TiN phase demonstrated the nitridation of titanium after sintering. Moreover, considering the short processing time and the low concentration of N₂ in the mixed gas, it was speculated that the nitriding reaction proceeded rapidly in the gas, given by²⁰

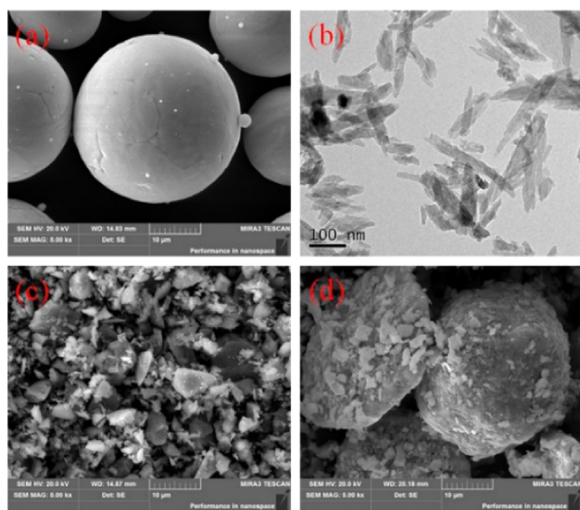


Figure 1. Micromorphologies of (a) Ti6Al4V, (b) HA, (c) TiB₂, and (d) their mixture after milling.

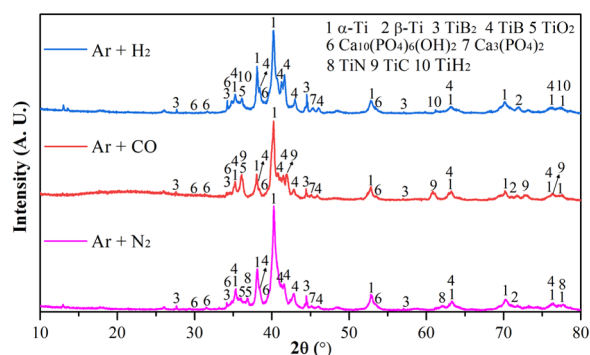


Figure 2. XRD patterns of the composites obtained by microwave sintering in different atmospheres.

The nitride formed inside the bulk was probably a result of precipitation upon cooling because the solubility of N in Ti reduced sharply at lower temperatures.²¹ Nitrogen is an α -stabilizing element, which can cause lattice distortion at the interface between oxide and metal, resulting in recrystallization against the inward migration of oxygen into the titanium matrix.²² Along with the formation of TiN, the α -Ti phase was reduced. Based on the XRD results, there existed the following orientation relationships between the crystal lattices of TiN and the α -Ti(N) solid solution: (110), [110] TiN || (0001), [1120] α -Ti(N).²³ Besides these main phases, the other minor phases included TiB₂ and TiB, which was formed due to the reaction between TiB₂ and Ti in the alloy matrix, expressed as²⁴



The titanium oxide (TiO₂) was also identified by the XRD pattern. Its formation was believed to be a result of the decomposition of HA during sintering, which led to the emission of H₂O as an oxidant of Ti, given by⁹



Another reason for the presence of titanium oxide was considered to be associated with the reaction between HA and Ti in the alloy due to the strong oxidation tendency of titanium atoms at the interface of HA/Ti or in the metal matrix

in association with the diffusion of interstitial oxygen atoms.²⁵ Obviously, it was difficult to prevent the formation of TiO₂ even for sintering within high-purity protective or inert gas, e.g., Ar (>99.99%).^{5,25} Along with the decomposition of HA, another product, calcium phosphate (Ca₃(PO₄)₂, also known as β -TCP), was identified by the XRD pattern in Figure 2, in agreement with the previous study.²⁶ It is worth mentioning that the existence of titanium in the alloy would facilitate the transition of HA to phosphate as titanium has the potential to lower the decomposition temperature of HA.

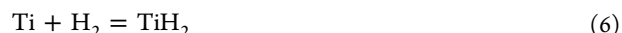
As discussed above, the oxidation of titanium existed when the composite was prepared in the mixed gas of Ar + N₂. This phenomenon was also common in pure Ar.⁵ For eliminating the potential negative impact of the oxygen in the protective gas, some reducing gases, such as CO and H₂, may be introduced. Figure 2 also shows the XRD pattern of the composite obtained by sintering in the mixed gas of Ar + CO. Compared with the case in the mixed gas of Ar + N₂, a new phase, TiC, due to the carbonization of titanium was mainly observed at 36.5 and 62° in the XRD pattern. The reaction occurred as follows²⁷



It indicated that there existed obvious adsorption of CO and migration of C into the composite surface. In addition, the peak of TiO₂ varied compared with the composite prepared in the mixed gas of Ar + N₂. This observation was because of the reaction between TiO₂ and CO, given by¹⁴



Note that the product, Ti₂O, was not present in the XRD pattern due to its low content. When sintering was performed in the mixed gas of Ar + H₂, another phase, TiH₂, was observed with weakened reflections from the main components of the composite. This hydriding reaction is expressed as follows²⁸



TiH₂ is brittle and thermally stable at low temperatures. The sintering of titanium could be accelerated by the diffusion of hydrogen atoms from TiH₂, along the α -Ti grain boundaries. During cooling, a part of TiH₂ was decomposed to Ti and H₂.²⁸ As a result, the reflection from the titanium matrix phase

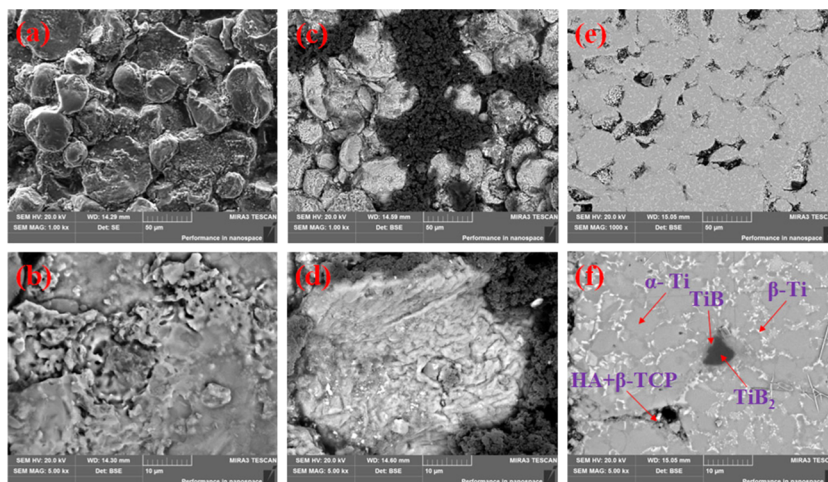


Figure 3. SEM micrographs of the composites obtained by microwave sintering in different atmospheres: (a, b) Ar + N₂, (c, d) Ar + CO, and (e, f) Ar + H₂. Note that in the former two cases, the composite components were not marked because of their unclear and difficult differentiation.

was lowered. Another reason for the change in the peak intensity could be related to the transition from β -Ti to α -Ti during cooling because of the higher hydrogen diffusion rate in β -Ti atoms than that in α -Ti atoms, which will broaden the stability region of the β -Ti phase.²⁹ From the above analysis, it was concluded that the atmosphere mainly controlled the phase transition associated with the alloy matrix in the composite.

Figure 3 shows the microstructures of the composites obtained by microwave sintering of the powder mixtures in different atmospheres. According to Figure 3a,b, after sintering in the mixed gas of Ar + N₂, the composite exhibited a loose structure. The particles of the alloy matrix still remained relatively independent, with clear boundaries between each other. There were some small particles located between the matrix components. According to the EDS analysis, they were composed of HA and its decomposition products (mainly β -TCP). The presence of TiN and HA decomposition products as secondary phases hindered the sintering process, leading to a low density.³⁰ From Figure 3c,d, the impact of CO in the mixed gas on the sintering was evident. The carbonization caused the microstructural color of the sample to change from gray to black. The EDS analysis confirmed that all of the dark regions consisted of the very high content of TiC, while the remaining gray areas maintained the main composition of the alloy matrix. It revealed that a small concentration of CO would lead to the apparent carbonization of the sample, which caused an even looser structure, as proved by the independent particles observed in Figure 3. As shown in Figure 3e,f, the addition of H₂ in the mixed gas produced a more compact structure. It was mainly constituted by the titanium alloy matrix, HA and TiB₂. The microstructure remained integrated with the lowest porosity. The α -Ti phase (dark color, dominant) and β -Ti phase (gray, minor) were found to be dominant in the particles. TiB was located in a boundary zone between TiB₂ and the matrix. The formation of TiB would contribute to the microstructural integration of the sample by strong chemical bonding, reducing the mechanical and thermophysical differences between the two components. It also acted as a "bridge" between the matrix and the surrounding HA particles. Overall, the microstructures of the composites were sensitive to the compositions of the mixed gases, especially those consisting of N₂ or CO whose excessive addition would lead to more serious nitridation or carbonization, producing loose structures. The mixed gas of Ar + H₂ is recommended for ensuring good sintering and thus densification of the composites.

Figure 4 summarizes the phase transformations and microstructural evolutions during the microwave-assisted fabrication of boronized Ti6Al4V/HA composites in different atmospheres. In terms of phase transformation, sintering in the different sintering atmospheres led to distinct product compositions. As discussed before, TiN, TiC, and TiH₂ were formed in the mixed gases of Ar + N₂, Ar + CO, and Ar + H₂, respectively. It should be pointed out that TiN and TiC have a much stronger microwave absorptivity than TiH₂. Hence, more microwave energy was absorbed in them, causing selective thermal effect, which, in turn, promoted their generations. It explained the noticeable observation of TiN and TiC in the corresponding XRD patterns (Figure 2) and SEM micrographs (Figure 3). Meanwhile, the generations of these compounds restrained the production of TiB layer, which was intensified by the "lens effect" of the microwave electric

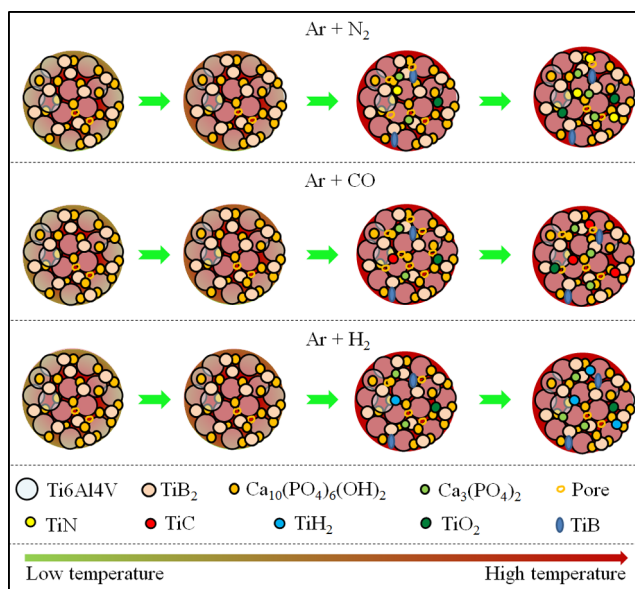


Figure 4. Schematic illustration of phase transformations and microstructural evolutions of the composites obtained by microwave sintering in different atmospheres.

field.³¹ For this reason, the loose microstructures of the composites were more apparent when sintered in mixed gases of Ar + N₂ and Ar + CO. On the other hand, the phase components were intertwined and distributed relatively evenly in the composite synthesized in the mixed gas of Ar + H₂, in spite of the existence of incompletely eliminated interfaces and a few entrapped micropores due to the gas emission from the partial decomposition of HA to β -TCP (eq 3)³² and to the different coefficients of thermal expansion of the alloy matrix and HA ($8.2 \times 10^{-6}/^{\circ}\text{C}$ for Ti vs $16 \times 10^{-6}/^{\circ}\text{C}$ for HA).^{33,34} Note that as a result of the selective thermal effect, the microwave could contribute to the low decomposition of HA because of its poor microwave absorptivity.³⁵ Volumetric heating might also occur during the process as the alloy matrix particles had sizes that matched with the corresponding micrometer-scale skin depth of microwave, enabling heating of all matrix particles. The combined microwave selective and volumetric thermal effects could result in a more efficient fabrication of the composite under microwave irradiation than the conventional approach, as verified by the significant reductions of sintering temperature and time (approximately 200 $^{\circ}\text{C}$ and over 1.5 h) in relevant previous studies.^{31,36}

Figure 5 shows the bulk densities of the composites obtained by microwave sintering in different atmospheres. The composite obtained in the mixed gas of Ar + CO had the

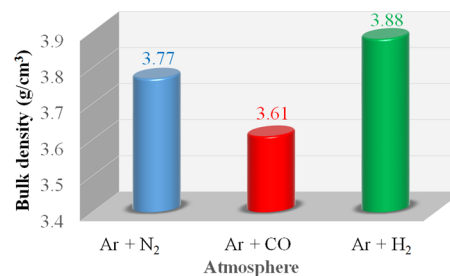


Figure 5. Comparison of bulk densities of the composites obtained by microwave sintering in different atmospheres.

lowest bulk density. This finding was consistent with the microstructural changes observed in the SEM micrographs (Figure 3), which show that after sintering in the mixed gas of Ar + CO, the composite had the loosest structures with independent matrix particles as a result of carbonization. This was followed by the composite prepared in the mixed gas of Ar + N₂, which caused a similar loose structure due to the nitridation effect of the gas during sintering. It modified the composition and structure of the resulting composite. The addition of H₂ to Ar had a much weaker influence on the structure of the composite, which can be confirmed by its high bulk density and very similar microstructure to those of raw materials, especially Ti6Al4V.⁷

Figure 6 shows the porosities of the composites obtained by microwave sintering in different atmospheres. As expected, the

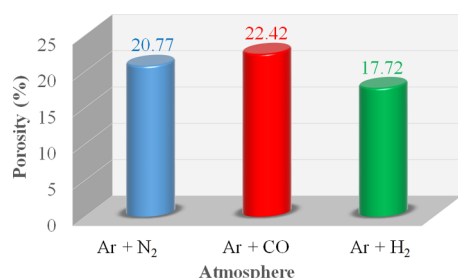


Figure 6. Comparison of porosities of the composites obtained by microwave sintering in different atmospheres.

composite prepared in the mixed gas of Ar + CO had the highest porosity, followed by those obtained in the mixed gases of Ar + N₂ and Ar + H₂. This order was in agreement with the changing trend of bulk density. Compared with the porosities of similar products reported in the literature,¹⁰ the values in the present study were higher, especially for the composites prepared in the presence of CO and N₂.

Figure 7 shows the values of the compressive strength of composites obtained by microwave sintering in different

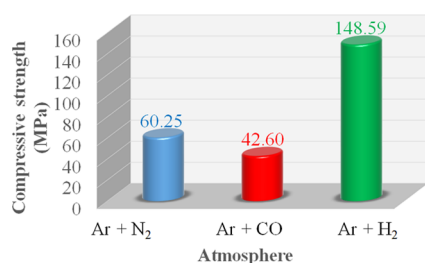


Figure 7. Comparison of compressive strength of the composites obtained by microwave sintering in different atmospheres.

atmospheres. It was found that the composites obtained in the mixed gas Ar + H₂ presented the highest compressive strength of 148.59 MPa. For those prepared in the mixed gases of Ar + N₂ and Ar + CO, however, the counterparts were only 60.25 and 42.60 MPa, respectively. Obviously, the atmosphere had a great impact on the compressive strength of the composite, which was believed to be associated with the high sensitivity of the strength to porosity, in agreement with relevant previous studies.¹¹ In fact, there was an inverse relationship between the compressive strength and the porosity for titanium-based composite biomaterials.³⁷ It explained the much lower compressive strength of composites prepared in

the mixed gases of Ar + N₂ and Ar + CO. It should be pointed out that for typical load-bearing implant applications, the compressive strength is usually at least 77 MPa.³¹ From this perspective, only the composite fabricated in the mixed gas of Ar + H₂ met the standard.

Figure 8 shows the comparison of the compressive moduli of the composites obtained by microwave sintering in different

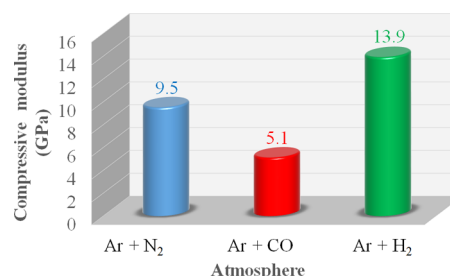


Figure 8. Comparison of compressive moduli of the composites obtained by microwave sintering in different atmospheres.

atmospheres. The compressive modulus had the same trend as the compressive strength due to the strong influence of porosity and phase composition.¹¹ The compressive moduli of the composites obtained in the mixed gases of Ar + N₂, Ar + CO, and Ar + H₂ were 9.5, 5.1, and 13.9 GPa, respectively, all meeting the requirement for load-bearing implants.³⁸

Figure 9 shows the values of Vickers microhardness of the composites obtained by microwave sintering in different

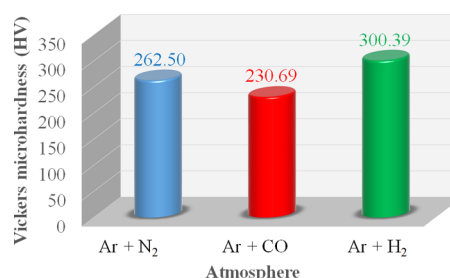


Figure 9. Comparison of Vickers microhardness of the composites obtained by microwave sintering in different atmospheres.

atmospheres. It was obvious that the composite fabricated in the mixed gases of Ar + CO displayed the lowest microhardness. The generation of TiC induced weak interfacial bonds between the alloy matrix and other components. There would be embrittlement of the composite due to an uneven distribution of the TiC cluster and thus a decrease in microhardness. The composite fabricated in the mixed gas of Ar + N₂ displayed higher microhardness in spite of its loose structure, resulting from the formation of high-microhardness TiN.³⁹ For the composite fabricated in the mixed gas of Ar + H₂, it had the highest microhardness of 300.39 HV, which was determined by the matrix of Ti6Al4V intensified by TiB because of its closer value to that of the alloy.⁴⁰ In general, the microhardness obeyed the same trend as compressive strength.

Figure 10 compares the water contact angles of the composites obtained by microwave sintering in different atmospheres. It is known that the water contact angle is an indicator of the wettability of a biomaterial. According to Figure 10, all of the composites exhibited the angles far less than 90°, showing their good hydrophilicities. The composite

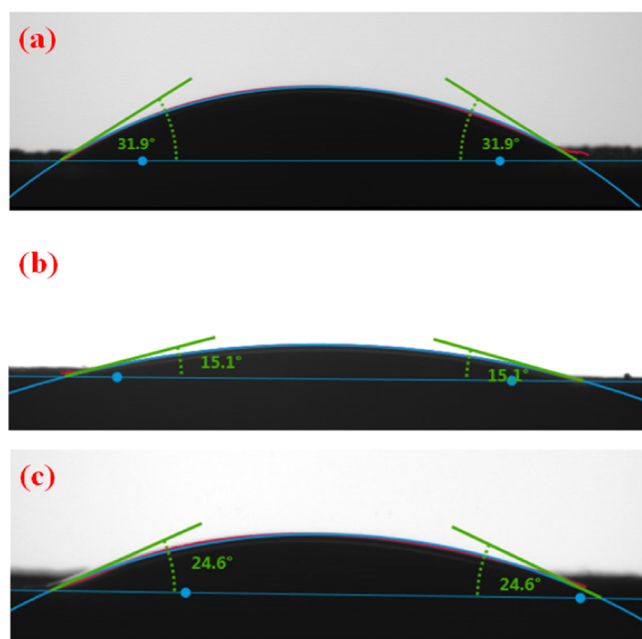


Figure 10. Comparison of water contact angles of the composites obtained by microwave sintering in different atmospheres: (a) Ar + N₂, (b) Ar + CO, and (c) Ar + H₂.

obtained in the mixed gas of Ar + N₂ possessed a low water contact angle (31.9°), basically in agreement with the findings in relevant studies.³⁹ This result partially confirmed the good biocompatibility of TiN.⁴¹ In addition, because the nitrided surface could improve the adhesion of fibroblast cells,⁴² the composite had the potential to be used as an implant material with better hydrophilicity than that obtained in pure Ar. For the other atmospheres, the introduction of CO and H₂ resulted in even lower angles (15.1 and 24.6°, respectively). This phenomenon was obvious in association with the formations of TiC and TiH₂ in the sintering process.

Overall, the properties of the composites had a strong dependence on the sintering atmosphere. They showed the following order of mechanical performance: Ar + H₂ > Ar + N₂ > Ar + CO. In addition, after sintering in the above mixed gases, their wettabilities appeared to be excellent, as demonstrated by the low water contact angles. The boronized Ti6Al4V/HA composite obtained in the atmosphere consisting of both Ar and H₂ exhibited the optimal mechanical properties and wettability, meeting the corresponding requirements of most load-bearing implantation applications, such as dental implantation, which is one of the main methods for repairing the missing teeth.³¹ In fact, it possessed higher compressive strength and modulus than those of the similar product reported in the literature (148.59 vs 93 MPa, 13.9 GPa vs 2.9 MPa, respectively).⁵ It may also have very attractive biological properties, which have been partially verified by the desirable biological activities of relevant Ti6Al4V-based composites with similar compositions.^{5,32} A detailed examination of the biological properties of the composite is ongoing.

4. CONCLUSIONS

This study explored the effect of atmosphere on the fabrication of boronized Ti6Al4V/HA composites by microwave sintering of the mixture of Ti6Al4V alloy, TiB₂, and HA at 1050 °C for 30 min in the mixed gases of Ar + N₂, Ar + CO, and Ar + H₂,

respectively. It was shown that the atmosphere impacted greatly the phase compositions and microstructures of the composites. For sintering in the mixed gas of Ar + N₂, TiN was formed due to the nitridation effect. For the case involving CO, the formation of TiC due to carbonization was observed. The presence of H₂ in the atmosphere had a slight effect on the phase composition of the resulting composite. In association with the above phase transformation, the composite obtained in the mixed gas of Ar + CO presented the loosest structure, followed by those fabricated in the mixed gases of Ar + N₂ and Ar + H₂. Because of the phase transformations and microstructural evolutions during sintering, the composites obtained in the mixed gases had the following order in terms of mechanical performance: Ar + H₂ > Ar + N₂ > Ar + CO. All of them had very low water contact angles (≤31.9°), indicating their good potential biocompatibilities after nitridation, carbonization, and hydrogenation. Particularly, the composite fabricated in the mixed gas of Ar + H₂ had the highest compressive strength (148.59 MPa), compressive modulus (13.9 GPa), and Vickers microhardness (300.39 HV), all showing high sensitivity of the porosity. Moreover, it exhibited excellent wettability with water contact angle of only 24.6°. The results indicated that the sintering atmosphere consisting of Ar and H₂ was optimal for producing boronized Ti6Al4V/HA composites with desirable mechanical properties and wettability, which paves the way for the development of high-quality load-bearing implant materials, such as those for dental implantation.

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work was partially sponsored by the Science and Technology Planning Project of Hunan Province, China,

under Grant 2019RS2008 and the Fundamental Research Funds for the Central Universities of Central South University under Grant 2018zzts040.

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